ELECTRICAL CONDUCTIVITIES OF THE SALT SOLUTIONS CONTAINING AGAR.

By Eiichi IWASE.

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The fact that the gelatine-sol containing salt does not change its electric conductivity on gelatinisation was already noticed by Arrhenius[1]. Laing and McBain[2] observed that there is no distinction in electric conductivity between soap sol and gel at the same concentration and temperature. Soap, however, is a so-called colloidal electrolyte and differs somewhat from a hydrophile colloid. Hatschek and Humphry[3] have recently reported that the conductivity of agar, water and copper sulphate mixture exhibits on gelatinising a slight but measurable alteration. My experiments have been undertaken to test such a case, and are described in the following lines.

Powdered agar from Merck was dispersed in distilled water or in aqueous salt solution by heating in a vessel provided with a condenser on a water bath. Special precaution was taken to prevent the evaporation of the water during the dispersion and the measurement. The electrodes of the conductivity cell were made of moderately thick well platinized platinum plates and wires. The measurements were carried out in a thermostat of $50°\pm0.05°$C. Being cooled by water from outside of the conductivity cell, sol was transformed into gel always in the same condition. Two percent $CuSO_4 \cdot 5H_2O$ solution prepared at 30° was diluted up to 1/32 percent. 25 c.c. of these aqueous salt solutions were taken, and 0.5 gr. agar was added to each of them and dispersed as above mentioned. The conductivities were measured of these aqueous solutions and agar solutions in sol and gel states. The results are shown in Table 1.

TABLE 1.

Grams of $CuSO_4 \cdot 5H_2O$ in 100 c.c. of water	Specific conductivity (mho $\times 10^6$)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
2	1011	1016	1020	4
1	598.8	606.9	609.7	2.8
1/2	353.4	388.1	390.6	2.5
1/4	209.1	252.9	255.4	2.5
1/8	122.9	170.6	171.8	1.2
1/16	70.71	122.7	123.6	0.9
1/32	40.70	100.1	101.3	1.2
Distilled water	3.039			

(1) Arrhenius, *Oefvers Stockholm Akad.*, 6 (1887), 121.
(2) Laing and McBain, *J. Chem. Soc.*, 117 (1920), 1503.
(3) Hatschek and Humphry, *Trans. Faraday Soc.*, 20 (1924), 18.

The same experiments were undertaken for other salts than $CuSO_4$, viz. K_2SO_4, KCl, KI, NaCl and KCNS solutions and the results are shown in Tables 2, 3, 4, 5, and 6 respectively. The data given in Table 2 are depicted in Fig. 1.

TABLE 2.

Conc. of K_2SO_4 normal	Specific conductivity (mho × 10^5)		
	Aqueous solution	Agar solution	
		Sol	Gel
0.2	3014	—	—
0.175	2685	—	—
0.15	2353	2270	—
0.125	2011	—	—
0.1	1656	1596	—
0.075	1289	—	—
0.05	898.5	869.2	—
0.025	481.7	486.6	490.0

TABLE 3.

Conc. of KCl millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	417.6	465.8	468.3	2.5
17.5	366.2	—	—	—
15.0	315.1	369.0	370.7	1.7
12.5	264.2	—	—	—
10.0	213.6	273.0	275.2	2.2
7.5	164.2	—	—	—
5.0	109.6	176.2	177.6	1.4
2.5	57.11	126.2	127.5	1.3
1.25	29.09	99.06	100.2	1.1
0.625	15.60	—	—	—

TABLE 4.

Conc. of KI millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	418.3	463.9	465.9	2.0
17.5	239.2	415.4	417.4	2.0
15.0	317.7	367.7	370.0	2.3
12.5	266.6	—	—	—
10.0	216.2	272.6	274.3	1.7
7.5	162.6	—	—	—
5.0	110.4	175.9	176.7	0.8
2.5	56.20	126.6	127.4	0.8
1.25	31.35	101.7	102.5	0.8
0.625	15.50	—	—	—

TABLE 5.

Conc. of NaCl millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.0	356.0	409.1	410.7	1.6
17.5	313.1	366.7	369.1	2.4
15.0	269.1	—	—	—
12.5	226.4	285.0	285.8	0.8
10.0	183.5	245.3	246.3	1.0
7.5	138.8	—	—	—
5.0	94.08	160.4	161.2	0.8
2.5	48.90	117.7	118.4	0.7
1.25	25.76	96.25	97.10	0.7
0.625	13.87	—	—	—

TABLE 6.

Conc. of KCNS millimol/litre	Specific conductivity (mho × 10^5)			
	Aqueous solution	Agar solution		
		Sol	Gel	Difference
20.14	393.4	440.5	442.8	2.3
17.6225	345.5	—	—	—
15.105	298.5	352.3	354.8	2.5
12.5875	250.2	—	—	—
10.07	201.2	259.4	261.0	1.6
7.5525	152.9	—	—	—
5.035	103.2	168.7	169.9	1.2
2.5175	52.92	—	—	—
1.2588	27.30	96.74	97.07	0.3
0.6294	15.70	—	—	—

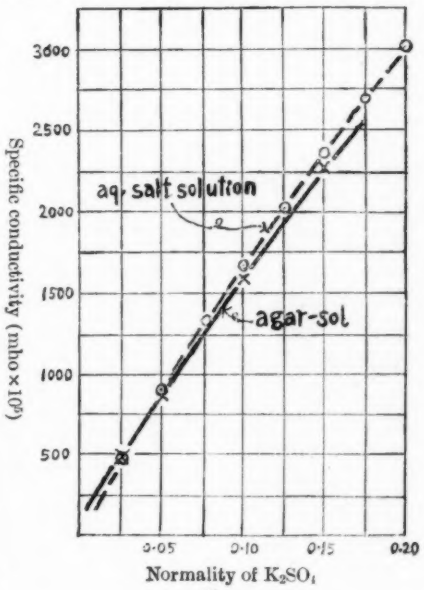

Fig. 1.

The conductivity of agar dispersed in distilled water has also been measured and the results are as follows. On ignition the agar has left ashes amounting from 3.5 to 4.0 percent.

TABLE 7.

Gram of agar in 25 c. c. of water	Specific conductivity (mho × 10^5)		
	Sol	Gel	Difference
0.1	18.45	18.19	−0.26
0.2	33.34	33.09	−0.25
0.3	47.53	47.38	−0.15
0.4	61.14	61.29	+0.15
0.5	73.77	74.47	+0.70
0.7	95.94	97.36	+1.42
1.0	130.0	132.5	+2.5

All the measurements, in which 0.5 gr. agar were dispersed in 25 c.c. of salt solutions, have confirmed the results observed by Hatschek and Humphry with regard to conductivity alteration on sol-gel transformation, and at the same time support Prof. P.P. von Weimarn's opinion on this phenomena[1], which read "by the aggregation or growth of particles during gelation and the consequent reduction in surface, adsorbed electrolyte might be liberated, which would account for the higher conductivity of the gel." When we assume the agar sol and gel are heterogeneous system and the conductivity of agar-water-salt system is almost all ascribed to the dissolved salt, then we are capable of calculating the quantity of electrolyte adsorbed on the surface of agar particles. The value of conductivity of agar dispersed in pure water was subtracted from that of agar dispersed in salt solution, and the salt concentration corresponding to this conductivity value can be obtained from the curve of conductivity–salt concentration in pure aqueous solution which we can easily draw by the direct determination. The difference between the salt concentration thus obtained and that of the original may

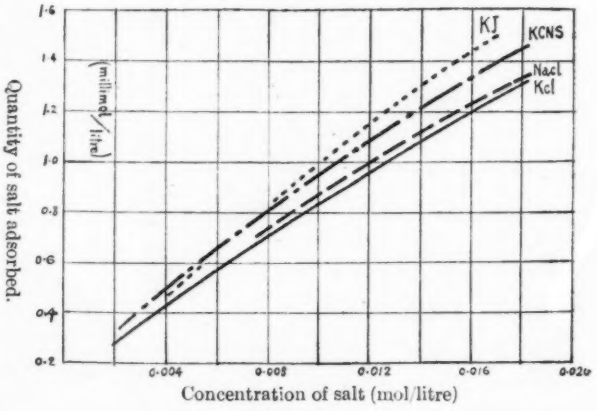

Fig. 2.

(1) *Trans. Faraday Soc.* **20** (1924), 29.

be regarded as the adsorbed quantity of the salt on the agar particles. Fig. 2 shows the adsorption of salts due to two percent agar sols.

The author wishes to express his sincere thanks to Prof. J. Sameshima for his kind guidance throughout the present research. The author's thanks are also due to Prof. P. P. von Weimarn for his kind advices.

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THE PHOTOCHEMICAL REACTIONS OF COLOURING MATTERS. I. THE REVERSIBLE PHOTOCHEMICAL REACTION OF MALACHITE GREEN.

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As is well known, colouring matters have played important rôles in the developement of photochemistry both from technical and scientific standpoints, for most of them are more or less sensitive to light and moreover their colour changes offer very convenient analytical methods in spite of complexity of the molecules. Indeed the bleaching effect of light on colouring matters has been very often investigated, and the results of these investigations accord at one point that most of these reactions are photocatalytic. While there are so many photocatalytic reactions in general, very few reversible photochemical reactions are known. Very simple photochemical reactions, such as those of tautomeric changes, will perhaps be favourable for the study of fundamental laws of photochemistry, provided that it is furnished with an easy and simple analytical method.

Berl,[1] Lassareff,[2] and Gebhard[3] formerly studied on the reversibility of methylene blue and Chevreul[4] on Prussian blue. Later J. Lifschitz and Joffé[5] described about photochemical molecular rearrangements in triphenylmethane series in the case of leucocyanides and carbinol bases of the dyes in the solutions of alcohols, ether, chloroform and aqueous mineral acids. A similar reaction was reported by Holmes[6] who used triphenylmethane sulphonic acid.

(1) Berl, *Ber.*, **43** (1910), 164.
(2) Lassareff, *Z. physik. Chem.*, **78** (1912), 651.
(3) Gebhard, *Z. physik. Chem.*, **79** (1912), 639.
(4) Chevreul, *Fortschritte der Physik*, (1894), 206.
(5) Lifschitz and Joffé, *Ber.*, **52** (1919), 1919; *Z. physik. Chem.*, **97** (1921), 426.
(6) Holmes, *J. Am. Chem. Soc.*, **44** (1922), 1002.

For the purpose of looking for a reversible photochemical reaction I have tried to expose aqueous solutions of various colouring matters contained in a quartz glass tube to the light of a quartz mercury lamp, and carefully measured their colour changes, using Nutting's spectro-photometer. In the course of these experiments, I have found that the colour of malachite green solution, contrary to expectation, became more intense after the exposure to the light of the mercury lamp. Repeating the same experiment with the dye in presence of various chemicals, I found that the dye solution, which was beforehand decolourised by adding alkali, regained its green colour when exposed to the light of the lamp, and loses its colour again in the dark. This reversible colour change of malachite green solution may be suitably observed in a quartz glass vessel illuminated with the light of iron or carbon arc, but the reaction occurs neither with diffused daylight nor with the light of ordinary electric lamp. Intense direct sunlight is able to cause the reaction even in a glass vessel.

Although the similar phenomena were observed in other colouring matters of triphenylmethane group such as fuchsin, methylviolet etc, the present study is concerned only with the experiments which were carried out with malachite green.

Experimental.

In the first place, velocities of the colour changes of malachite green solutions were determined in the following three cases, in using Nutting's spectro-photometer: 1) Decolourisation in alkaline medium. (NaOH was added) 2) Regaining of the colour when exposed to the light of quartz-mercury-vapour-lamp. 3) Reversed decolourisation in the dark.

Experiment 1. 0.0218 gr. of malachite green (from Grueber in Germany) was dissolved in one litre of distilled water and diluted to the four times of its volume.(1) To each 50 c.c. of this solution was added respectively 5 c.c. of NaOH solution of the concentrations of 0.05, 0.03, 0.025, 0.02, 0.015, 0.010, 0.005 and 0.003 normal and the velocities of decolourisation of these solutions were observed.

The absorption tubes of the photometer were furnished with water jackets through which water of constant temperature was allowed to circulate from a thermostat in order to keep the system in a constant temperature. The light absorption was observed at the spectrum region of wave length 600 $\mu\mu$, where exists the absorption maximum of malachite green and, therefore, observations may be very conveniently carried out even in such a dilute solution as this.

(1) If the solution be in larger concentration, white precipitates would be produced when alkali is added, therefore the experiment must be carried out within the limit of solubility of this difficultly soluble, colourless matter.

As the concentration of the colouring matter is very small in comparison with that of NaOH, we can practically take this reaction as that of first order, leaving, as the further question, the doubt about which of catalytic or of second order is the real nature of this reaction.

The concentration of the substance, the absorption of which is to be measured, can be expressed as follows,

$$C=\frac{-2\log\cos\alpha}{Ed} \quad \cdots\cdots\cdots\cdots\cdots\cdots(1)$$

where α is the angle of the rotation of Nicol's prism, C the concentration of the colouring matter, E the extinction coefficient of the solution, d the thickness of the liquid layer.

Therefore, the velocity constant of the reaction, $K=\frac{1}{t}\log\frac{C_0}{C}$ can be expressed in terms of $\cos\alpha$ as follows,

$$K=\frac{1}{t}\{\log(-\log\cos\alpha_0)-\log(-\log\cos\alpha)\}\cdots\cdots(2)$$

TABLE 1.

t	α	$-\log\cos\alpha$	$\log(-\log\cos\alpha)$	$\log\frac{C_0}{C}$	$K=\frac{1}{t}\log\frac{C_0}{C}$
0	85.0	1.0597	0.025	—	—
3	79.0	0.7194	$\bar{1}$.857	0.168	.056
6	70.6	0.4787	$\bar{1}$.680	0.315	.058
10	61.5	0.3213	$\bar{1}$.507	0.518	.052
16	47.5	0.1703	$\bar{1}$.230	0.795	.050
28	22.0	0.0328	$\bar{2}$.516	0.509	.054

The control observation which was specially planned, showed that the extinction coefficient was constant throughout the concentration used, that is, the Beer's law holds.

The velocity increases with the concentration of NaOH linearly as may be seen in Table 2.

TABLE 2.

NaOH	0.03 N	0.025 N	0.02 N	0.015 N	0.01 N	0.005 N	0.003 N
$K\times10^3$	86	74	54	43	30	16	9.2

Experiment 2. The solution of malachite green which was previously decolourised by adding NaOH, was exposed to the light of a quartz-mercury-vapour-lamp (from Heraeus of Hanau, Germany) at the distance of 15 cm.

and after various intervals of time, a definite quantity of the solution was taken out of the reaction vessel and light absorption of this solution was measured in the same manner as in Experiment 1.

The mercury lamp with its illuminating part of 1.65 cm. in length was lighted with 100 volts D. C., the current being 3 amps. throughout the experiment. In ten minutes after the lamp had been started, its light became constant in intensity. Both of the reaction vessel and light thermostat were made of cylindrical tubes of quartz glass, the former being inserted in the latter, through which water of constant temperature was circulated from a larger thermostat by means of a pump. The solution was agitated with a stirrer during the exposure.

I have prepared three kinds of malachite green solutions with different concentrations, one of these (solution A) is in about the same concentration as in the Exp. 1, while those of the other two (solution B and C) are respectively in the two thirds and one half of the first. To each 250 c.c. of the solution A, B and C, 5 c.c. of 0.01 N. NaOH was added. The solutions thus decolourized were exposed to the light of the lamp, the intensity of which, being found to be too strong was reduced to one fourth by inserting a rotating sector with two 45° apertures (800–1000 rotations per min.) between the light source and the reaction vessel and the change of colour was observed, keeping temperature constant at 25°.

In this case, the velocity constant of the light reaction was calculated in the following way: in the first place, it was considered that the amount of light sensitive substances which suffer changes by light is proportional to the light energy absorbed and consequently the reaction velocity can be put,[1]

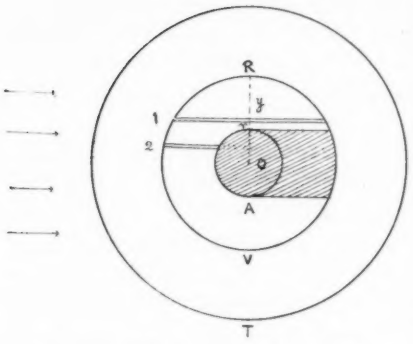
$$\frac{dM}{dt} = KA = KS(I_0 - I) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

and if Beer's law holds

$$\frac{dM}{dt} = KS(I_0 - I_0 e^{-idc}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where M is the amount of the substance, and A the quantity of absorbed light. This relation is satisfied only in such a case that the reacting system is contained in a rectangular vessel and exposed to parallel beams of light which are perpendicular to the wall of the vessel. In the present experi-

(1) Literatures on photochemical kinetics give us two different conceptions: 1. The equations of reaction velocity are same for photochemical and dark reaction. 2. The amount transformed is proportional to the absorbed light quantity. The light reaction of malachite green, however, being unimolecular, both of these conceptions lead us to the same conclusion.



Horizontal section of the apparatus.
T : Thermostat vessel.
V : Reaction vessel. (Radius R.)
A : Agitator. (Radius r.)

Fig. 1.

ment, however, the cylindrical vessel having been used, following considerations will be necessary for the calculation of the velocity constant.

Now if we take the elementary slices 1 and 2 in Fig. 1, their volumes are,

$$2\sqrt{R^2-y^2}\,h\,dy \quad \text{and}$$
$$\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}h\,dy \ldots(5)$$

respectively, and the light absorbed by them are

$$I_0\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\}h.\,dy \text{ and}$$
$$I_0\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\}h.\,dy$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where b is the initial concentration of the substance, x the concentration of the substance formed, h the height of the part of the vessel exposed to the light, R and r the radii of the vessel and the agitator.

The equation (3) can be then, put as follows :

$$\frac{dM}{dt}=\frac{dV(b-x)}{dt}=K_0\Big[2\int_r^R I_0\{1-e^{-i\,2\sqrt{R^2-y^2}(b-x)}\}h.\,dy$$
$$+2\int_0^r I_0\{1-e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}\}h.\,dy\Big] \ldots\ldots\ldots\ldots\ldots(7)$$

where $$e^{-i\,2\sqrt{R^2-y^2}(b-x)}=1-i\,2\sqrt{R^2-y^2}(b-x)+\frac{[i\,2\sqrt{R^2-y^2}(b-x)]^2}{1\cdot2}-\ldots(8)$$

$$e^{-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)}=1-i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)$$
$$+\frac{[i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}(b-x)]^2}{1\cdot2}-\ldots\ldots\ldots\ldots\ldots(9)$$

and if i or b is very small, we can neglect higher terms and consequently the equation (7) becomes

$$\frac{d(b-x)}{dt}=\frac{K_0}{V}2I_0h\Big[\int_r^R i\,2\sqrt{R^2-y^2}.dy+\int_0^r i\{\sqrt{R^2-y^2}-\sqrt{r^2-y^2}\}dy\Big](b-x)$$
$$=a\text{ constant}\times(b-x)=K(b-x) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

and finally the equation of the velocity constant can be put as

$$K=\frac{1}{t}[\log b-\log(b-x)]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where b and x can be expressed in terms of log cosα as in Experiment 1.

Although the extinction coefficient of the solution could not yet been determined, it is evident, however, that the concentration of the light sensitive substance is very small in this experiment and higher terms of the equations (8) and (9) may be neglected.

Velocity constants were thus calculated according to the equation (11) and pretty constant values were obtained as will be seen in Table 3, etc, giving rather smaller values at the beginning of the reaction.

It must be noted here that, the thermostat vessel used being cylindrical, the refraction of light beams at the wall of the vessel must be taken into consideration in the above calculations, but this was neglected for the sake of simplification, incident rays being assumed to be parallel.

TABLE 3.

Time (min)	2	4	6	8	10	12	14	16	18
$K \times 10^3$ (A)	35	44	51	53	51	51	50	—	—
$K \times 10^3$ (B)	35	43	43	51	51	53	59	—	53
$K \times 10^3$ (C)	39	41	45	52	58	61	59	54	—

In order to study the effect of the concentration of alkali, 5 c.c. of 0.03 and 0.02 N. NaOH were respectively added to each 250 c.c. of the solution A and the same experiment as mentioned above was done. It was, however found that in these cases there was good accordance of the observed values with those of Table 3, that is to say, the light reaction is independent of the concentrations of alkali present.

TABLE 4.

Time (min)	1	2	4	6	8	10	12	16
$K \times 10^3$ (0.02)	34	37	43	47	51	56	58	56
$K \times 10^3$ (0.03)	34	35	36	39	45	51	57	56

The temperature coefficient was then determined at 25° and 35° in using the solution A added with 0.01 N. NaOH and it was proved that the light reaction is practically not effected by the raise of temperature, at this interval, although more accurate experiment on this account will be necessary for its support.

TABLE 5.

Time (min)	2	4	6	8
$K \times 10^3$ (25°)	34	51	49	49
$K \times 10^3$ (35°)	32	42	49	49

Finally the effect of light intensity on the light reaction was also examined. The light of three different intensities of 1/2, 1/4 and 1/8 were applied to the solution C added with 0.01 N. NaOH, and it was found that the velocity of the light reaction is exactly proportional to the light intensity as will be expected.

Experiment 3. Five c.c. of 0.01 N. NaOH was added to each 50 c.c. of the solution A and C and these mixtures which show moderate reaction velocities were transferred into absorption tubes, after having exposed to the light of the mercury lamp until the green colour of these solutions took maximum intensity, and then the light absorption was measured in definite time interval in exactly the same manner as in Experiment 1. (Table 6)

TABLE 6.

Time (min.)	10	20	30	40	60	90	100	120	150	170	180
$K \times 10^3$ (sol. A)	76	62	—	58	56	—	57	—	56	—	55
$K \times 10^3$ (sol. C.)	53	58	59	55	59	59	—	55	52	52	—

The reaction velocity increases linearly with the concentrations of NaOH added as was proved in Experiment 1, only slightly differing in the angle of inclination. (Table 7)

TABLE 7.

$K \times 10^3$	76	65	40	30	19	7.8	5.6
Conc. of alkali	0.03	0.025	0.02	0.015	0.01	0.005	0.003

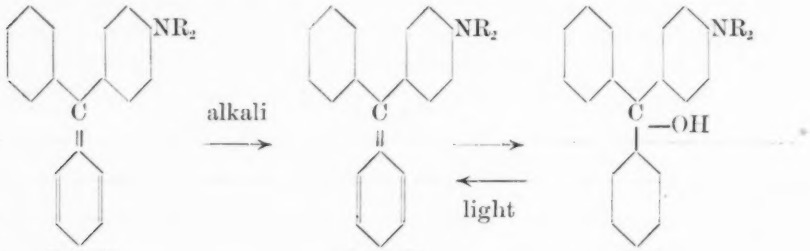
Discussion of Experimental Results. In Experiment 1, the decolourisation velocity of malachite green in presence of alkali was proved to be proportional to the concentration of sodium hydroxide added and the reaction may be taken as of first order, on the contrary to the results obtained by Mueller[1] and by Gerlinger,[2] who calculated the velocity constant by electrochemical method. But it must be taken in mind that my experiment has been carried out in excess of alkali in comparison with that of light sensitive substance. If this photochemical reversible reaction of malachite green, however, is considered to be a tautomeric change of colour-base as was indicated by Hantzsch and Osswald,[3] it seems more probable that the reaction is of first order, alkali acting itself catalyticaly.

Experiment 3 may be discussed exactly the same way as in Fxperiment

(1) W. J. Mueller, *Ber.*, **43** (1910), 2609.
(2) P. Gelinger, *Ber.*, **37** (1904), 3958.
(3) A. Hantzsch u. G. Osswald, *Ber.*, **33** (1900), 278.

1, if we consider that the coloured substance produced by light (Exp. 2) is a ammoniumbase, its decolourising velocity in the dark increasing linearly with the concentration of alkali added.

Hantzsch and Osswald have proved that in malachite green as well as in triphenylmethane dyes two kinds of modification are possible, one being in coloured and unstable ammonium-base and the other colourless and stable pseudo-ammonium-base type (carbinol type):



$R_2N.Cl$
Salt of dye

$R_2N.OH$
Coloured ammonium base

R_2N
Colourless pseudo ammonium base

If it is allowed to adopt these formulae, the coloured substance which is produced by the action of light can be considered to be this unstable coloured ammonium-base, and the other formed by the decolourisation in the dark will then be the stable colourless pseudo-ammonium-base.

In Experiment 2 it was observed that the linear relation holds between the intensity of the light and the reaction velocity. I have carried out the further experiments with the intention of finding out the limit at which the equation of zero order would be satisfied when factors such as thickness of liquid layer and the light intensity were changed. But sufficient data for this purpose have not yet been obtained.

The temperature coefficient of the velocity constant of the light reaction per ten degrees has been shown to be unity in the interval between 25° and 35°C, and this fact can be taken as a strong support that the reaction which we are now dealing with, is of pure photochemical one. The velocity of the dark reaction, which is quite insignificant as long as the concentration of alkali is small, increases rapidly in raising its concentration as well as temperature, while the light reaction is neither influenced by the temperature nor by the concentration of alkali.

So far as the visible part of the spectrum concerned, the absorptions are

quite same in both cases of original colouring matter solution and the photo-product. Absorption spectrum of ultraviolet region was also studied in using the quartz spectrograph (Adam Hilger), and iron arc as the light source. But I failed to obtain a good photography of the absorption spectrum; the concentration of the substance having been very small, no distinct absorption band was to be detected on the plates.

As for the wave lengths of the most effective light, it will require further studies. Only it may be said that the optimum part lies in the ultraviolet region of spectrum, because the solution contained in an ordinary glass tube is not effected by illuminating with the light of iron arc, while it is easily coloured if a quartz glass vessel is used. Intense direct sunshine or the light from a mercury lamp of high intensity has shown, however, the colouring effect even in an ordinary glass vessel.

The author desires to express his best thanks to Dr. S. Iimori of the Institute, and to Dr. N. Yamaga of the Research Laboratory of the Hiratsuka Explosive Factory of the Imperial Japanese Navy for helps and facilities which they have given him in completing this research.

Summary.

1. The photochemical reversible reaction of the alkaline solution of malachite green was studied with the quartz-mercury-lamp, and its nature was discussed.

2. The reaction velocities were determined both in the light and the dark reaction, using Nutting's spectro-photometer. The former is proportional to the intensity of light and the latter to the concentration of the alkali added.

3. The temperature coefficient of the reaction velocity of the light reaction was found to be unity at the interval between 25° and 35° C.

4. Equation of the reaction of first order was derived with approximation for the light reaction.

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THE EFFECT OF ALKALI ON THE OXIDATION OF SODIUM SULPHITE WITH AIR.

By **Susumu MIYAMOTO.**

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It was described in the previous paper[1] that C. C. Palit and N. R. Dhar found[2] that some carbohydrates are oxidized with air in the presence of sodium sulphite and that the oxidation is accelerated on adding caustic alkali. They further measured the amount of sodium sulphite oxidized with air in the presence of carbohydrates and found that on adding caustic alkali the velocity of the oxidation of sodium sulphite decreases.[3] But it is not clear whether the retardation is the effect of the induced reaction or caustic alkali.

S. L. Bigelow[4] studied the catalytic action of many substances on the oxidation velocity of sodium sulphite with air, but the effect of alkali was not studied well. A. Titoff[5] studied the same phenomena also. In his experiment the oxidation was carried out in water which had been previously saturated with oxygen, that is, he studied the oxidation as a homogeneous reaction.

The purpose of this study is to know the effect of alkali more precisely by a modified method, and to discuss the promoting action of alkali on the induced oxidation, found by Dhar and Palit.

Experimental. The experimental procedure was quite the same with that described in the previous paper, only a large test-tube (diameter, 3 cm.) was used instead of an Erlenmeyer flask (100 c.c.), which was used in the previous experiment, for the vessel in which the oxidation takes place. Air, washed by acidified potassium dichromate solution and alkali, was passed at constant velocity into the solution of sodium sulphite of known concentration. The total volume of the solution was made to 40 c.c. in each case. After t minutes the air current was stopped and the total amount of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back by means of sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.09962 normal which is equivalent to the

(1) S. Miyamoto, This journal, **2** (1927), 40
(2) Palit and Dhar, *J. Phys. Chem.*, **29** (1925), 799; **30** (1926), 939.
(3) *J. Phys. Chem.*, **30** (1926), 948.
(4) Bigelow, *Z. physik. Chem.*, **26** (1898), 493.
(5) Titoff, *Z. physik. Chem.*, **45** (1903), 641.

amount of sodium sulphite; k is calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$, and $v_{calc.}$ is obtained by $v_{calc.}=v_0-kt$, using the mean value of k.

TABLE 1.

Temp: 20°C. Air: 7.78 litres per hour. $C_{NaOH}=0$.

t min.	v c.c.	$v_{calc.}$ c.c.	k
0	16.71	—	—
10	13.42	13.41	0.329
15	11.87	11.76	0.322
20	10.03	10.11	0.334
30	7.40	6.81	0.310
0	29.16	—	—
8	26.48	26.52	0.335
10	25.75	25.86	0.341
12	25.12	25.20	0.337
15	24.05	24.21	0.341
24	21.49	21.24	0.320
0	38.64	—	—
9	35.73	35.67	0.323
12	34.54	34.68	0.342
22	31.56	31.38	0.322
		Mean:	0.330

Table 1 shows that the amount of sodium sulphite oxidized with air is independent of its concentration. This fact coincides with that obtained by Bigelow,[1] and can be explained by assuming that the velocity of the dissolution of oxygen into the solution is much slower than that of the oxidation of sodium sulphite.

The Effect of Alkali. The oxidation in sodium hydroxide solution of various concentrations was measured. The results are shown in Table 2.

(1) Bigelow, *Z. physik. Chem.*, 26 (1898), 518.

TABLE 2.

Temp: 20°C. Air: 7.78 litres per hour.

C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
	0	13.23	—	—		0	14.25	—	—
0.02888	9	10.52	10.55	0.301	0.7219	8	12.57	12.55	0.210
	15	8.87	8.76	0.297		12	11.68	11.69	0.214
	25	5.63	5.78	0.304		14	11.30	11.27	0.210
	30	4.23	4.29	0.300		16	10.66	10.84	0.224
	35	3.20	2.80	0.287		25	9.10	8.92	0.206
			Mean	0.298				Mean	0.213
	0	12.05	—	—		0	12.37	—	—
0.05173	9	9.41	9.57	0.293	1.1011	9	10.77	10.85	0.178
	12	8.71	8.74	0.278		12	10.26	10.34	0.176
	15	7.95	7.91	0.273		15	9.86	9.83	0.167
	20	6.60	6.53	0.273		20	9.12	8.99	0.163
	30	4.11	3.77	0.265		30	7.52	7.30	0.162
			Mean	0.276				Mean	0.169
	0	12.18	—	—		0	12.17	—	—
0.1810	9	9.70	9.79	0.276	1.810	9	11.26	11.28	0.1011
	12	8.90	9.00	0.273		12	11.01	11.00	0.0967
	15	8.35	8.20	0.255		15	10.59	10.69	0.1053
	20	6.88	6.88	0.265		20	10.24	10.19	0.0965
	30	4.50	4.23	0.256		30	9.32	9.20	0.0950
			Mean	0.265				Mean	0.0989
	0	13.98	—	—					
0.5173	10	11.66	11.67	0.232					
	12	11.10	11.21	0.240					
	15	10.42	10.51	0.237					
	20	9.56	9.36	0.221					
	30	7.29	7.05	0.223					
			Mean	0.231					

Thus the sodium hydroxide diminishes the oxidation velocity of sodium sulphite. This will be explained by assuming the caustic alkali diminishes the dissolution velocity of oxygen into the solution. This assumption will also explain why the oxidation velocity of ferrous hydroxide[1] with air decreases with the increase of the concentration of caustic alkali, although its reducing power increases. Anyhow the increase of the induced oxidation of carbohydrates in the presence of sodium sulphite on adding caustic alkali is not due to the increase of the velocity of the primary reaction. Sodium

(1) S. Miyamoto, This journal, 2 (1927), 40.

hydroxide can be regarded as one of the substances which accelerate the induced reaction but not the primary reaction. The mechanism of this kind of promoters of induced reaction can be explained by the theory of the transference of active states.[1]

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are shown in Table 3. The effect of temperature was very small.

$$\frac{k_{30°}}{k_{20°}}=\frac{0.345}{0.330}=1.05, \quad \frac{k_{40°}}{k_{39°}}=\frac{0.382}{0.345}=1.11 \quad \text{when } C_{NaOH}=0$$

$$\frac{k_{30°}}{k_{29°}}=\frac{0.265}{0.231}=1.15, \quad \frac{k_{40°}}{k_{30°}}=\frac{0.301}{0.265}=1.14 \quad \text{when } C_{NaOH}=0.5173 \text{ Normal}$$

TABLE 3.

Air : 7.78 litres per hour.

Temp. C.	C_{NaOH} normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C	0	0	13.69	—	—
		9	10.52	10.58	0.352
		12	9.37	9.55	0.360
		15	8.50	8.51	0.346
		20	7.00	6.79	0.335
		30	3.78	3.11	0.330
				Mean	0.345
30°	0.5173	0	13.69	—	—
		9	11.18	11.30	0.279
		12	10.57	10.51	0.260
		15	9.73	9.71	0.264
		20	8.42	8.39	0.264
		30	6.01	5.74	0.256
				Mean	0.265
40°	0	0	11.84	—	—
		9	8.24	8.40	0.400
		12	7.35	7.26	0.374
		15	5.82	6.11	0.401
		20	4.52	4.20	0.366
		25	2.61	2.29	0.369
				Mean	0.382
40°	0.5173	0	11.41	—	—
		9	8.62	8.70	0.310
		12	7.64	7.80	0.314
		15	7.07	6.89	0.289
		20	5.07	5.39	0.311
		30	3.00	2.38	0.280
				Mean	0.301

(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, 4 (1926), 257.

The Effect of the Velocity of Air Passed. Table 4 is the results measured when air was passed at the rate of 6.67 and 10 litres per hour. By comparing this with Table 1, it will be seen that the oxidation velocity increases with the increase of the velocity of air current passed.

TABLE 4.

Temp: 20°C. $C_{NaOH}=0$.

Air litres per hour	t min.	v c.c.	$v_{calc.}$ c.c.	k
6.67	0	13.57	—	—
	9	10.87	10.87	0.300
	12	9.84	9.97	0.311
	15	9.20	9.07	0.291
	20	7.18	7.57	0.313
	30	5.00	4.57	0.286
			Mean	0.300
10.0	0	12.98	—	—
	9	9.68	9.79	0.367
	12	8.65	8.73	0.361
	15	7.70	7.67	0.352
	20	5.98	5.90	0.350
	30	2.75	2.36	0.341
			Mean	0.354

Summary.

1. The oxidation velocity of sodium sulphite with air was independent of its concentration.

2. Caustic alkali diminishes the velocity of the oxidation.

3. The effect of temperature was small.

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THE FORMATION OF OXY-DERIVATIVES OF DIPHENYLENE OXIDE FROM RESORCIN.

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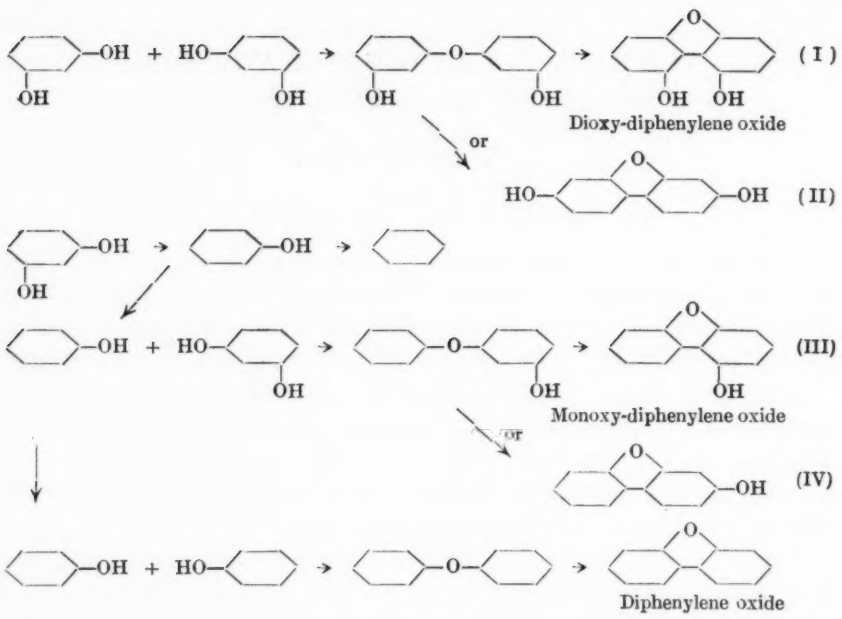
It was reported[1] that resorcin undergoes a certain reduction and condensation under the influence of blue oxide of tungsten between 500° and 550°, giving rise to the formation of a new compound which was supposed to be 2,6-dioxydiphenyl. With the view of ascertaining this constitution and whether there is any other product or not, and also of inquiring into the mechanism of this formation, this reaction was further examined by the suggestion of Professor B. Kubota.

The reaction was carried out exactly in the same manner as described in the previous paper. After the whole of the reaction products was subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction, the remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued. By means of this steam distillatin it was found that there existed two products, one of which distils with steam though it goes on very slowly, and the other remains in the residual liquid. The former, melting at 138–138°.5, gave a monomethoxy-derivative $C_{12}H_7O(OCH_3)$ by being treated with sodium hydroxide and dimethylsulphate, whilst when heated with zinc dust diphenylene oxide was produced. The latter, melting at 241–242°, gave a dimethoxy-derivative $C_{12}H_6O(OCH_3)_2$ and diphenylene oxide by being treated in the same way. These facts lead us to suppose that the one compound melting at 138–138°.5 is evidently a monoxy-diphenylene oxide which contains two hydrogen atoms less than dioxy-diphenyl in the previous paper and the other melting at 241–242° a dioxy-diphenylene oxide.

Thus it seems to me that the production of benzene, phenol, diphenylene oxide, monoxy- and dioxy-diphenylene oxide may be regarded as the result of the normal action (dehydration) of the catalyst, accompanied by its secondary action (reduction), the processes of which being represented by the following schemes:

(1) Kubota, Fujimura and Akashi, *Scientific Papers of the Institute of Physical and Chemical Research*, 2 (1925), 185.



The well known formation of diphenylene oxide from phenol by means of lead oxide[1] or aluminium oxide[2] and also from diphenyl ether by means of heating[3] is suggestive of a remarkable tendency of the newly combining phenyl groups occupying ortho position with respect to the bridge oxygen atom. On the other hand, absorption curves show in their forms much resemblance to those of o-oxy-derivatives of diphenyl but not to those of p-oxy-derivatives[4], and those of acetyl derivatives are in good agreement with that of diphenylene oxide. Besides, it has been shown[4] that phenyl malonic acid was produced on oxidising the hexahydro-derivative of the compound melting at 138–138°.5. From this fact it is clear that the compound melting at 138–138°.5 is 2-oxydiphenylene oxide (formula III). From this point of view the formula I (2,2′-dioxydiphenylene oxide) ~~becomes highly probable as that of the dioxy-diphenylene oxide)~~ becomes highly probable as that of the dioxy-diphenylene oxide.

(1) Graebe, *Ber.*, **7** (1874), 396.
(2) Sabatier and Maihe, *Compt. rend.*, **151** (1910), 429; *Bull. soc. Chim.*, **11** (1912), 843; *Compt. rend.*, **155** (1912), 260; **158** (1914), 608.
(3) Graebe u. Ullmann, *Ber.*, **29** (1896), 1876.
(4) Kubota, Fujimura and Akashi, loc. cit.

Experimental.

Monoxy-diphenylene Oxide. *The Methoxy-derivative.* Oxydiphenylene oxide (0.1 gr.) obtained by passing resorcin vapour over blue oxide of tungsten at 500–550° as described in the paper cited above, was dissolved in a sodium hydroxide solution and a drop of dimethyl sulphate was added. The solution was warmed, when some white crystals separated out. Being recrystallised from dilute alcohol, it separated out in small plates melting at 93–94.° Yield 0.08 gr. It is soluble in alcohol and ether, but insoluble in water. 2.503 mg. and 2.398 mg. substance gave 3.086 mg. and 2.862 mg. AgI. (Found: $-OCH_3=16.29$ and 15.77. $C_{12}H_7O(OCH_3)$ requires $-OCH_3=15.66\%$.)

From this result the formula $C_{12}H_7O(OH)$ becomes more probable as that of the compound melting at 138–138°.5 than $C_{12}H_8(OH)_2$ which was reported in the previous paper.

Nitro-derivative. Oxy-diphenylene oxide (16 mg.) was dissolved in glacial acetic acid and some drops of concentrated nitric acid were added. The solution on being warmed on the water bath yielded 10 mg. of fine yellow crystals. Upon recrystallisation from hot petroleum ether, it separated out in small prisms becoming dark brown at about 200° and melting with decomposition at 216–217°. 1.300 mg. gave 0.112 c.c. of N_2(20°, 754 mm.). (Found: $N=9.87$, $C_{12}H_6N_2O_6$ requires $N=10.22\%$). It is soluble in alcohol and in almost all other organic solvents, but insoluble in water. This substance appears to be 3,5-dinitro-oxydiphenylene oxide.

Dioxy-diphenylene Oxide. The reaction products which were obtained by passing resorcin vapour over the catalyst at 500–550° were subjected to steam distillation until no crystalline substance deposited in the condenser and the distillate showed no marked phenolic reaction. The remainder in the distilling flask was made strongly acidic with hydrochloric acid and the steam distillation was continued so long as oxy-diphenylene oxide came out. The residual liquid was filtered from a tarry matter while still hot and was allowed to stand a mean while, when some brown prisms separated out. These were dissolved in hot water, treated with animal charcoal and recrystallised, but the faint brown colour was not removed off. It is soluble in alcohol, ether and hot water, but scarcely soluble in cold water, thuogh it is more soluble than oxy-diphenylene oxide. With a ferric chloride solution it gives a green colour turning to a light brown on the addition of sodium carbonate solution. It becomes almost colourless at 100° and melts at 241–242°. On being dehydrated over P_2O_5 at 100° under a diminished pressure, 5.31 mg. of the substance lost 0.22 mg. of water. (Found: $H_2O=4.31$; $C_{12}H_8O_2 1/2H_2O$ requires $H_2O=4.15\%$).

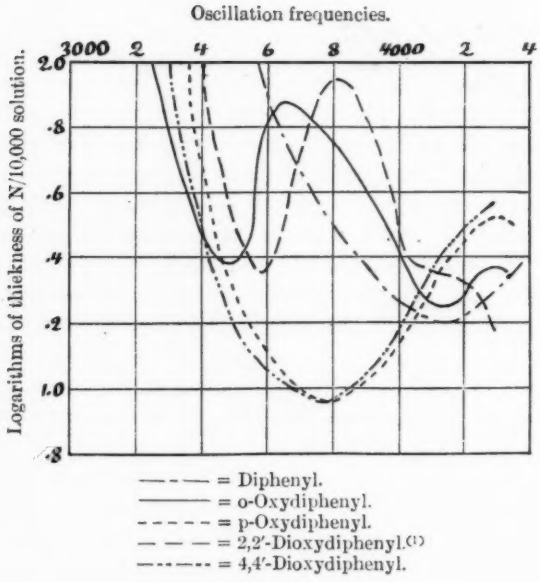


Fig. 1.

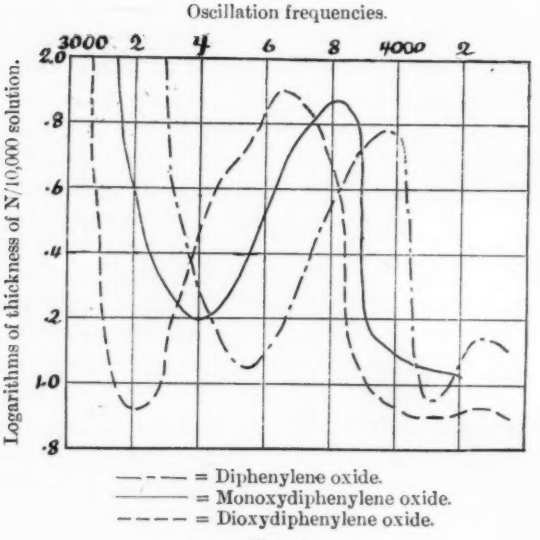


Fig. 2.

Molecular weight was determined by K. Rast's method. 0.14 mg. of substance in 1.94mg. of camphor gave $\Delta t = -13.°0$. (Found: M=210. $C_{12}H_8O_3$ requires M=200.)

The Dimethoxy-derivative. The dioxy-diphenylene oxide was treated with sodium hydroxide and dimethyl sulphate as described in the case of oxy-diphenylene oxide, when fine crystals were obtained. It was recrystallised from dilute alcohol, when it separated out in small plates melting at 150°. It is soluble in alcohol and ether, but insoluble in water. 2.123 mg. of substance gave 4.348 mg. AgI. (Found: $-OCH_3=27.06$. $C_{12}H_6O(OCH_3)_2$ requires $-OCH_3=27.20\%$).

The Acetyl-derivative. The dioxy-diphenylene oxide was warmed on the water bath with an excess of acetyl chloride, and that part of acetyl chloride, which was not used in the acetylation was for the most part driven off by diminishing pressure while still hot, when a residue consisting

(1) In practice, its dimethoxy derivative was observed, for dioxydiphenyl was not easily obtained.

of fine crystals was obtained. It was recrystallised from dilute acetic acid, when it separated out in small plates melting at 138°. 0.190 mg. of substance in 2.682 mg. of camphor gave $\Delta t = -10°.0$. (Found: M=283. $C_{12}H_6O(OCOCH_3)_2$ requires M=284.)

The Zinc Dust Distillation. The dioxy-diphenylene oxide was intimately mixed with zinc dust and was gradually heated in a small test tube, when a colourless oil solidifying to a crystalline state in the upper part of the tube was found to distil off. This product was washed with sodium hydroxide solution and was recrystallised from dilute alcohol, when it separated out in scaly crystals melting at 80–81°. Its properties were found in good agreement with those of diphenylene oxide.

Absorption Curve. The results of a comparative study of the absorption curves of diphenylene oxide, oxy-diphenylene oxide, dioxy-diphenylene oxide and their acetyl derivatives are shown in the figures which, as already pointed out, give an indication of the fact that the compound meltings at 138–138°,5 and at 241–242° are both derivatives of diphenylene oxide whose hydroxyl groups are attached to the ortho position with respect to the other phenyl group. The curves of the two acetyl derivatives of oxy-diphenylene oxides are not especially drawn in the diagram as they are superposed on that of diphenylene oxide. All observations of absorption spectra were made in alcoholic solutions.

The author's best thanks are due to Professor B. Kubota under whose kind guidance the present investigations were carried out.

Summary.

The substance which was formerly supposed as 2,6-dioxydiphenyl was shown to be 2-oxydiphenylene oxide (III).

A new phenol was obtained, the formula of which was shown to be dioxydiphenylene oxide $C_{12}H_6O(OH)_2$. Two hydroxy groups seem to be in 2 and 2′ positions from the mechanism of its formation and its absorption spectrum.

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